Supplementary Material (ESI) for Organic and Biomolecular Chemistry

A Deep Cavitand Catalyzes the Diels-Alder Reaction of Bound Maleimides

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Supplementary Information

Tabulated Kinetics Data

Adamantyl Maleimide **4**

Cavitand ***1***

[malemide] = 20.0 mM
[cavitand] = 4.0 mM
[anthracenemethanol] = 20 mM

time/min	[product]total/mM
0	0.000
21	0.226
290	2.285
1376	5.656
1761	7.376
2785	9.751
3272	10.588
4573	12.421
8483	15.882
10110	16.810
13360	17.805

k_{acc} = 0.259 M-1 min-1

Control

[malemide] = 12.4 mM
[anthracenemethanol] = 12.4 mM

time/min	[maleimide]/mM	1/[Mal] - 1/[Mal]$_0$
0	12.4	0.000
31	12.2	0.001
304	12	0.003
1388	10.85	0.012
1773	10.35	0.016
2798	10	0.019
3284	9.45	0.025
4590	8.55	0.036
8491	6.95	0.063
10124	6.15	0.082
13374	5.45	0.103

k_{uncat} = 0.0076 M-1 min-1

Acetanilide

[malemide] = 20.0 mM
[acetanilide] = 160 mM
[anthracenemethanol] = 20 mM

time/min	[maleimide]/mM	$1/[Mal] - 1/[Mal]_0$
0	20.00	0.0000
230	18.36	0.0045
520	19.48	0.0013
1915	17.93	0.0058
3405	17.00	0.0088
4935	15.85	0.0131
6015	15.33	0.0152

$k_{acetanilide}$ = 0.0026 M-1 min-1

*Cavitand **1** in benzene: no binding*

[malemide] = 20.0 mM
[cavitand] = 1.3 mM
[anthracenemethanol] = 20 mM

time/min	[maleimide]/mM	$1/[Mal] - 1/[Mal]_0$
0	20.000	0.000
1440	17.220	0.008
2940	14.348	0.020
5700	11.249	0.039
7440	9.107	0.060
10080	7.365	0.086

$k_{benzene}$ = 0.0080 M-1 min-1

Adamantylmethylmaleimide **5**

*Cavitand **1***

[malemide] = 20.0 mM
[cavitand] = 4.0 mM
[anthracenemethanol] = 20 mM

time/min	[product]total/mM
0	0.000
70	1.500
384	3.767
1389	13.267
1777	14.933
2987	16.600
4440	17.583

k_{acc} = 0.775 M-1 min-1

Control

[malemide] = 14.0 mM
[anthracenemethanol] = 14.0 mM

time/min	[maleimide]/mM	$1/[Mal] - 1/[Mal]_0$
0	14	0.000
78	13.7	0.002
966	10.1	0.028
1382	9.8	0.031
2524	7.3	0.066
4290	5.4	0.114
6953	3.75	0.195

k_{uncat} = 0.027 M-1 min-1

Cyclooctylmaleimide **6**

Cavitand ***1***

[malemide] = 20.0 mM
[cavitand] = 4.0 mM
[anthracenemethanol] = 20 mM

time/min	[product]total/mM
0	0.000
78	2.630
391	8.038
1394	15.052
1784	16.180
2994	18.184
4445	19.248

k_{acc} = 0.98 M-1 min-1

Control

[malemide] = 11.3 mM
[anthracenemethanol] = 11.3 mM

time/min	[maleimide]/mM	1/[Mal] - 1/[Mal]$_0$
0	11.3	0.000
81	11.15	0.001
971	9.45	0.017
1389	8.95	0.023
2529	7.65	0.042
4294	5.9	0.081
6957	4.8	0.120

k_{uncat} = 0.017 M-1 min-1

tert-Octylmaleimide **7**

Cavitand ***1***

[malemide] = 20.0 mM
[cavitand] = 4.0 mM
[anthracenemethanol] = 20 mM

time/min	[product]total/mM
0	0.000
26	0.148
297	1.077
1382	3.400
1767	3.759
2791	5.744
3277	6.315
4585	8.046
8487	10.876
10117	11.489
13367	13.010

k_{acc} = 0.143 M-1 min-1

Control

[malemide] = 14.2 mM
[anthracenemethanol] = 14.2 mM

time/min	[maleimide]/mM	1/[Mal] - 1/[Mal]$_0$
0	14.2	0.000
35	14.1	0.000
311	14	0.001
1394	13.25	0.005
1779	13	0.007
2805	12.45	0.010
3291	12.15	0.012
4595	11.6	0.016
8496	10.05	0.029
10131	9.6	0.034
13381	8.7	0.045

k_{uncat} = 0.0033 M-1 min-1

4-Cyclohexylphenylmaleimide **8**

Cavitand ***1***

[malemide] = 20.0 mM
[cavitand] = 4.0 mM
[anthracenemethanol] = 20 mM

time/min	[product]total/mM
0	0.000
28	0.376
403	5.908
1380	11.294
1847	12.463
2879	13.403
3235	13.841
4208	14.196

k_{acc} = 0.100 M^{-1} min^{-1}

Control

[malemide] = 18.5 mM
[anthracenemethanol] = 18.5 mM

time/min	[maleimide]/mM	$1/[Mal] - 1/[Mal]_0$
0	18.5	0.000
38	18.35	0.000
409	16.1	0.008
1375	11.4	0.034
1838	10.25	0.044
2873	8.6	0.062
3240	7.75	0.075
4215	6.95	0.090

k_{uncat} = 0.022 M-1 min-1